

2023 Semester 1 Main Examination

Faculty of Natural Sciences, Department of Chemistry

Qualification:	D. Analytical Chemistry	Date:	Fri 2 June 2023
Subject and Level:	Analytical Chemistry II	Venue:	NAT SC BLOCK
Subject Code:	ANAC 321/ANCH102	Time:	09:00 Hrs
Total Marks:	155	Duration:	3 Hours
Full Marks:	150	Examiners:	M M Shapi
Annexures:	Periodic table.		F T Zwane
No. of Pgs. incl. cover page:	18	Moderator:	N E Damoyi

Student Name:

Student's Signature:

Student Number:

Examiner's Signature:

Moderator's Signature:

Question	Q1	Q2	Q3	Q4							Total	Full Marks	%
Marks allocated	40	35	37	43							155	145	100%
Examiner													
Moderator													

For office use only:

INSTRUCTIONS TO STUDENTS:

1. Answer all questions in ink.
2. Write all answers in the answer book or question paper provided.
3. Non-programmable calculators may be used.
4. Do not turn over until permission is given.

QUESTIOIN 1: Neutralisation reactions

[40 Marks]

1.1 A 30.0 cm^3 of 0.020 M solution of NH_3 is titrated with 0.020 M solution of HCl . Calculate the pH of the solution after addition of the following volumes of titrant during titration. $K_a = 5.7 \times 10^{-10}$

1.1.1 5.00 cm^3 (6)

1.1.2 30.00 cm^3 (7)

1.1.3 37.00 cm³

(4)

1.2 With reasonable argument, predict whether the following solutions are acidic, neutral or basic. $K_{\text{aNH}_4^+} = 5.7 \times 10^{-10}$, $K_{\text{aHOAc}} = 1.75 \times 10^{-5}$, $K_{\text{w}} = 1.0 \times 10^{-14}$

1.2.1 0.100 M NaCl.

(2)

1.2.2 0.100 M NH₄OAc

(3)

1.2.3 0.100 M NaOAc

(3)

- 1.3 A buffer solution is 0,200 M in acetic acid (HOAc) and in sodium acetate. Calculate the pH change upon addition of 1.0 cm^3 of 0.100 M HCl to 10.0 cm^3 of this buffer solution.

(9)

- 1.4 Calculate the pH of a solution that is made up of 0.0600 M Na_2CO_3 and 0.030 M NaHCO_3 . $K_{a2} = 4.69 \times 10^{-11}$.

(6)

QUESTION 2: Complex Formation Titrations**[35 Marks]**

- 2.1** A solution containing a zinc ion was treated with EDTA at pH 6.0 ($\alpha_4 = 2.2 \times 10^{-5}$, $K_{MY} = 3.2 \times 10^{16}$). If the concentration of ZnY^{2-} was afterwards found to be $1.25 \times 10^{-2} M$, calculate the concentration of Zn^{2+} remaining uncomplexed. **(5)**

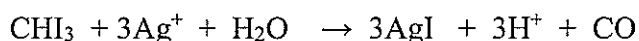
- 2.2** A solution contains 1.694 mg of $CoSO_4$ per millilitre. Calculate the volume of 0.008640 M EDTA needed to titrate the Zn^{2+} displaced by Co^{2+} following addition of an unmeasured excess of ZnY^{2-} to a 25.00 cm^3 aliquot of the $CoSO_4$ solution. The reaction is: $Co^{2+} + ZnY^{2-} \rightarrow CoY^{2-} + Zn^{2+}$. **(7)**

- 2.3** The cadmium and lead ions in a 50 cm³ sample required 40.09 cm³ of 0.004780 M EDTA for titration. A 75 cm³ portion of the same sample was made basic and treated with excess KCN, masking cadmium as Cd(CN)₄²⁻. This solution required 31.44 cm³ of the EDTA for titration. Calculate the concentration of Cd²⁺ and Pb²⁺ in the sample in parts per million
- (13)**

- 2.4** A 25.0 cm³ aliquot of 0.015 M Mg(NO₃)₂ was titrated with 0.010 M EDTA at pH 10 ($\alpha_4 = 0.35$; $K_{\text{MgY}} = 4.9 \times 10^8$). Calculate the pMg²⁺ after addition of 45.00 cm³ of EDTA.
- (10)**

QUESTION 3: Precipitation titrations.**[37 Marks]**

- 3.1 Distinguish between three precipitation methods. (6)
- 3.2 The Volhard method for determination employs the use of nitrobenzene. With the aid of equations explain why nitrobenzene is used. (3)
- 3.3 Write all the equations for the reactions taking place in the Volhard method including the reaction that is responsible for the red colour that is observed when Fe(III) is used as an indicator. (3)
- 3.4 The action of alkaline I_2 solution upon the rodenticide warfarin, $C_{19}H_{16}O_4$, results in the formation of 1 mole of iodoform, CHI_3 , for each mole of the parent compound reacted. Analysis of warfarin can then be based upon the reaction between CHI_3 and Ag^+ :

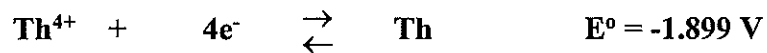


The CHI_3 produced from a 13.96 g sample was treated 25 cm³ of 0.02979 M $AgNO_3$ and excess Ag^+ was titrated with 2.85 cm³ of 0.05411 M KSCN. Calculate the percentage of warfarin in the sample. (10)

- 3.5** Calculate the pAg in the titration of 50 cm^3 of 0.050 M KI with 0.100 M AgNO_3 after addition of (i) 10 cm^3 , (ii) 25 cm^3 and (ii) 30 cm^3 . $AgI_{ksp} = 8.3 \times 10^{-17}$. **(15)**

QUESTION 4: Electrochemistry**[43 Marks]**

- 4.1.** An electrochemical cell contains a Thorium electrode setting in 1.00 M solution of Th^{4+} and a Galium electrode setting in a 1.00 M solution of Ga^{3+} .



- 4.1.1** Balance the overall **spontaneous** cell reaction. **(3)**

- 4.1.2** What is E° for this cell? **(2)**

- 4.1.3** What is the oxidizing agent of the reaction? **(2)**

- 4.1.4** What is the equilibrium constant (K_{eq}) for this reaction? **(4)**

- 4.2. Calculate (**against a SHE**) the potential of a mercury (II) electrode in a solution of black mercury sulfide, HgS which contains $4.54 \times 10^{-15} \text{ M S}^{2-}$, given that: (5)

$$K_{sp} \text{ for HgS} = 6.44 \times 10^{-53}$$



- 4.3 Membrane electrodes are specific to given ions but may be subject to interferences by other ions that may be present in the analysis solutions:

- 4.3.1 With the help of a suitable schematic diagram explain how the calcium (Ca^{2+}) liquid membrane electrode functions. (4)

4.3.2 The Ca^{2+} liquid membrane electrode is vulnerable to interferences by the presences of certain ions in an analysis sample. Name two (2) such ions that can cause major interferences. (2)

4.4 For the below unknown metal you are provided with the following data (measured against a Standard Hydrogen Electrode (SHE)):



Solution number	Concentration in Mol/L	E (in volts)
1	1.00×10^{-6}	-0.6246
2	1.00×10^{-5}	-0.5950
3	1.00×10^{-4}	-0.5654
4	1.00×10^{-3}	-0.5358

4.4.1 Plot a graph of $-\log [\text{M}^{n+}]$ (on the X-axis) against $-E$ (on Y-axis) on the provided graph paper. The following graph scales are recommended: (4)

X-axis: 2 cm = 1; starting from the bottom left hand corner.

Y-axis: 4 cm = 0.1; starting from the bottom left hand corner.

4.4.2 Use the graph in 4.4.1 to determine the number, n , of electrons in the above half reaction for the metal? (3)

4.4.3 Determine E° for the half reaction from your graph. (3)

4.4.4 Identify the metal ion in the half reaction using the table provided, giving two (2) reasons for your choice. (3)

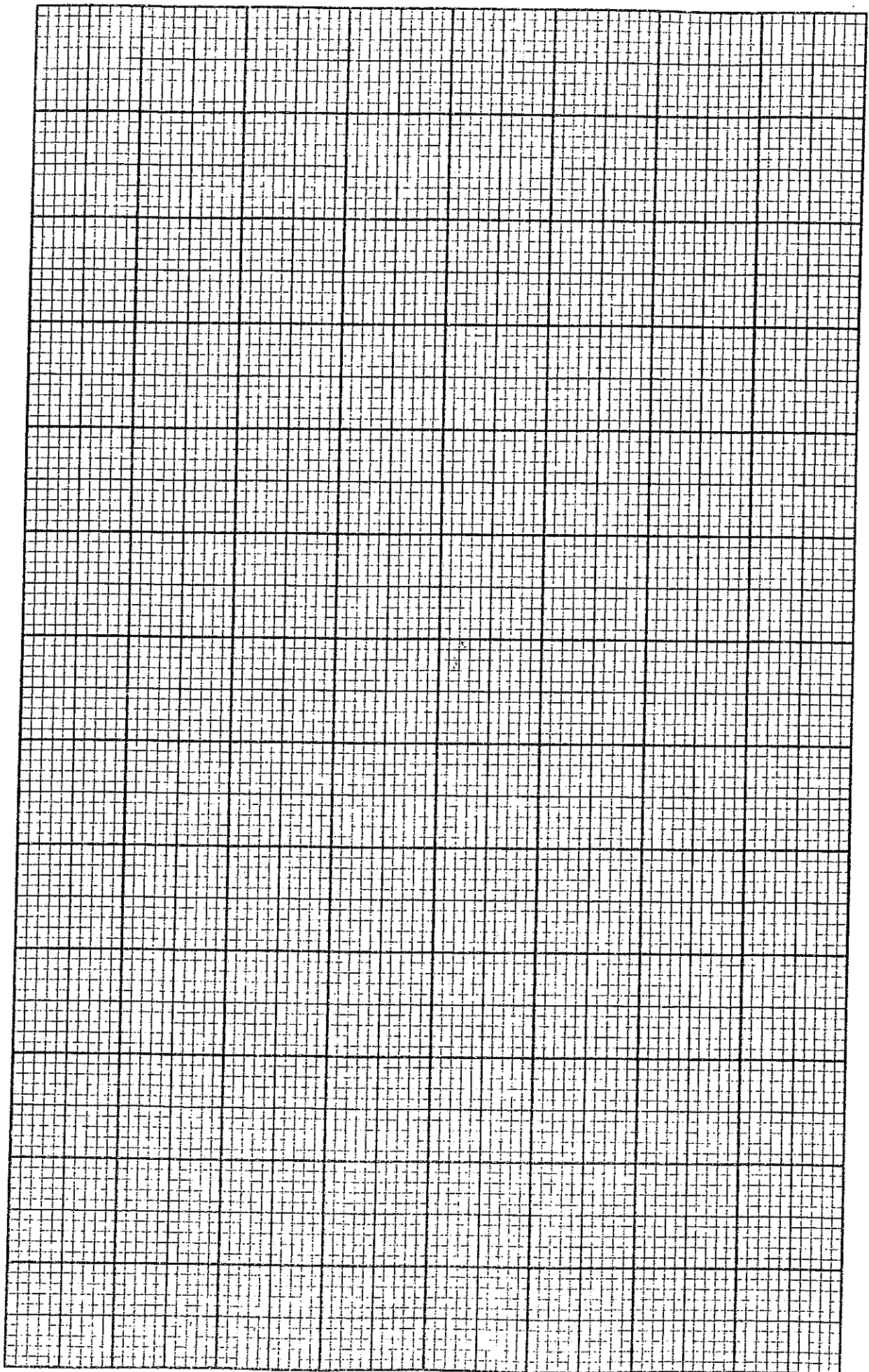


Table 2 (continued)
REDUCTION REACTIONS HAVING E° VALUES MORE POSITIVE THAN THAT OF THE
STANDARD HYDROGEN ELECTRODE

Reaction	E°, V	Reaction	E°, V
$2 \text{NO} + 2 \text{H}^+ + 2 \text{e} \rightleftharpoons \text{N}_2\text{O} + \text{H}_2\text{O}$	1.591	$\text{N}_2\text{O} + 2 \text{H}^+ + 2 \text{e} \rightleftharpoons \text{N}_2 + \text{H}_2\text{O}$	1.766
$\text{Bi}_2\text{O}_3 + 4 \text{H}^+ + 2 \text{e} \rightleftharpoons 2 \text{BiO}^+ + 2 \text{H}_2\text{O}$	1.593	$\text{H}_2\text{O}_2 + 2 \text{H}^+ + 2 \text{e} \rightleftharpoons 2 \text{H}_2\text{O}$	1.776
$\text{HBrO} + \text{H}^+ + \text{e} \rightleftharpoons 1/2 \text{Br}_2(\ell) + \text{H}_2\text{O}$	1.596	$\text{Co}^{3+} + \text{e} \rightleftharpoons \text{Co}^{2+} (2 \text{ mol/l } \text{H}_2\text{SO}_4)$	1.83
$\text{H}_2\text{IO}_6 + \text{H}^+ + 2 \text{e} \rightleftharpoons \text{IO}_3^- + 3 \text{H}_2\text{O}$	1.601	$\text{Ag}^{2+} + \text{e} \rightleftharpoons \text{Ag}^+$	1.980
$\text{Ce}^{4+} + \text{e} \rightleftharpoons \text{Ce}^{3+}$	1.61	$\text{S}_2\text{O}_8^{2-} + 2 \text{e} \rightleftharpoons 2 \text{SO}_4^{2-}$	2.010
$\text{HClO} + \text{H}^+ + \text{e} \rightleftharpoons 1/2 \text{Cl}_2 + \text{H}_2\text{O}$	1.611	$\text{OH}^- + \text{e} \rightleftharpoons \text{OH}^-$	2.02
$\text{HClO}_2 + 3 \text{H}^+ + 3 \text{e} \rightleftharpoons 1/2 \text{Cl}_2 + 2 \text{H}_2\text{O}$	1.628	$\text{O}_3 + 2 \text{H}^+ + 2 \text{e} \rightleftharpoons \text{O}_2 + \text{H}_2\text{O}$	2.076
$\text{HClO}_2 + 2 \text{H}^+ + 2 \text{e} \rightleftharpoons \text{HClO} + \text{H}_2\text{O}$	1.645	$\text{S}_2\text{O}_8^{2-} + 2 \text{H}^+ + 2 \text{e} \rightleftharpoons 2 \text{HSO}_4^-$	2.123
$\text{NiO}_2 + 4 \text{H}^+ + 2 \text{e} \rightleftharpoons \text{Ni}^{2+} + 2 \text{H}_2\text{O}$	1.678	$\text{F}_2\text{O} + 2 \text{H}^+ + 4 \text{e} \rightleftharpoons \text{H}_2\text{O} + 2 \text{F}^-$	2.153
$\text{MnO}_4^- + 4 \text{H}^+ + 3 \text{e} \rightleftharpoons \text{MnO}_2 + 2 \text{H}_2\text{O}$	1.679	$\text{FeO}_4^{2-} + 8 \text{H}^+ + 3 \text{e} \rightleftharpoons \text{Fe}^{3+} + 4 \text{H}_2\text{O}$	2.20
$\text{PbO}_2 + \text{SO}_3^{2-} + 4 \text{H}^+ + 2 \text{e} \rightleftharpoons \text{PbSO}_4 + 2 \text{H}_2\text{O}$	1.6913	$\text{O}(\text{g}) + 2 \text{H}^+ + 2 \text{e} \rightleftharpoons \text{H}_2\text{O}$	2.421
$\text{Au}^+ + \text{e} \rightleftharpoons \text{Au}$	1.692	$\text{H}_2\text{N}_2\text{O}_2 + 2 \text{H}^+ + 2 \text{e} \rightleftharpoons \text{N}_2 + 2 \text{H}_2\text{O}$	2.65
$\text{Ce}(\text{OH})^{3+} + \text{H}^+ + \text{e} \rightleftharpoons \text{Ce}^{3+} + \text{H}_2\text{O}$	1.715	$\text{F}_2 + 2 \text{e} \rightleftharpoons 2 \text{F}^-$	2.866
		$\text{F}_2 + 2 \text{H}^+ + 2 \text{e} \rightleftharpoons 2 \text{HF}$	3.053

Table 3
REDUCTION REACTIONS HAVING E° VALUES MORE NEGATIVE THAN THAT OF THE
STANDARD HYDROGEN ELECTRODE

Reaction	E°, V	Reaction	E°, V
$2 \text{H}^+ + 2 \text{e} \rightleftharpoons \text{H}_2$	0.00000	$\text{PbCl}_2 + 2 \text{e} \rightleftharpoons \text{Pb} + 2 \text{Cl}^-$	-0.2675
$\text{AgCN} + \text{e} \rightleftharpoons \text{Ag} + \text{CN}^-$	-0.017	$\text{H}_3\text{PO}_4 + 2 \text{H}^+ + 2 \text{e} \rightleftharpoons \text{H}_3\text{PO}_3 + \text{H}_2\text{O}$	-0.276
$2 \text{WO}_3 + 2 \text{H}^+ + 2 \text{e} \rightleftharpoons \text{W}_2\text{O}_5 + \text{H}_2\text{O}$	-0.029	$\text{Co}^{3+} + 2 \text{e} \rightleftharpoons \text{Co}$	-0.28
$\text{W}_2\text{O}_5 + 2 \text{H}^+ + 2 \text{e} \rightleftharpoons 2 \text{WO}_2 + \text{H}_2\text{O}$	-0.031	$\text{PbBr}_2 + 2 \text{e} \rightleftharpoons \text{Pb} + 2 \text{Br}^-$	-0.284
$\text{D}^+ + \text{e} \rightleftharpoons 1/2 \text{D}_2$	-0.0034	$\text{Tl}^+ + \text{e} \rightleftharpoons \text{Tl}(\text{Hg})$	-0.3338
$\text{Ag}_2\text{S} + 2 \text{H}^+ + 2 \text{e} \rightleftharpoons 2 \text{Ag} + \text{H}_2\text{S}$	-0.0366	$\text{Ti}^+ + \text{e} \rightleftharpoons \text{Ti}$	-0.336
$\text{Fe}^{3+} + 3 \text{e} \rightleftharpoons \text{Fe}$	-0.037	$\text{In}^{3+} + 3 \text{e} \rightleftharpoons \text{In}$	-0.3382
$\text{Hg}_2\text{I}_2 + 2 \text{e} \rightleftharpoons 2 \text{Hg} + 2 \text{I}^-$	-0.0405	$\text{TlOH} + \text{e} \rightleftharpoons \text{Tl} + \text{OH}^-$	-0.34
$2 \text{D}^- + 2 \text{e} \rightleftharpoons \text{D}_2$	-0.044	$\text{PbF}_2 + 2 \text{e} \rightleftharpoons \text{Pb} + 2 \text{F}^-$	-0.3444
$\text{Ti}(\text{OH})_3 + 2 \text{e} \rightleftharpoons \text{TlOH} + 2 \text{OH}^-$	-0.05	$\text{PbSO}_4 + 2 \text{e} \rightleftharpoons \text{Pb}(\text{Hg}) + \text{SO}_4^{2-}$	-0.3505
$\text{TiOH}^{3+} + \text{H}^+ + \text{e} \rightleftharpoons \text{Ti}^{3+} + \text{H}_2\text{O}$	-0.055	$\text{Cd}^{2+} + 2 \text{e} \rightleftharpoons \text{Cd}(\text{Hg})$	-0.3521
$2 \text{H}_2\text{SO}_3 + \text{H}^+ + 2 \text{e} \rightleftharpoons \text{HS}_2\text{O}_4^- + 2 \text{H}_2\text{O}$	-0.056	$\text{PbSO}_4 + 2 \text{e} \rightleftharpoons \text{Pb} + \text{SO}_4^{2-}$	-0.3588
$\text{P}(\text{white}) + 3 \text{H}^+ + 3 \text{e} \rightleftharpoons \text{PH}_3(\text{g})$	-0.063	$\text{Cu}_2\text{O} + \text{H}_2\text{O} + 2 \text{e} \rightleftharpoons 2 \text{Cu} + 2 \text{OH}^-$	-0.360
$\text{O}_2^- + \text{H}_2\text{O} + 2 \text{e} \rightleftharpoons \text{HO}_2^- + \text{OH}^-$	-0.076	$\text{Eu}^{3+} + \text{e} \rightleftharpoons \text{Eu}^{2+}$	-0.36
$2 \text{Cu}(\text{OH})_2 + 2 \text{e} \rightleftharpoons \text{Cu}_2\text{O} + 2 \text{OH}^- + \text{H}_2\text{O}$	-0.080	$\text{PbI}_2 + 2 \text{e} \rightleftharpoons \text{Pb} + 2 \text{I}^-$	-0.365
$\text{WO}_3 + 6 \text{H}^+ + 6 \text{e} \rightleftharpoons \text{W} + 3 \text{H}_2\text{O}$	-0.090	$\text{SeO}_3^{2-} + 3 \text{H}_2\text{O} + 4 \text{e} \rightleftharpoons \text{Se} + 6 \text{OH}^-$	-0.366
$\text{P}(\text{red}) + 3 \text{H}^+ + 3 \text{e} \rightleftharpoons \text{PH}_3(\text{g})$	-0.111	$\text{Ti}^{3+} + \text{e} \rightleftharpoons \text{Ti}^{2+}$	-0.368
$\text{GeO}_2 + 2 \text{H}^+ + 2 \text{e} \rightleftharpoons \text{GeO} + \text{H}_2\text{O}$	-0.118	$\text{Se} + 2 \text{H}^+ + 2 \text{e} \rightleftharpoons \text{H}_2\text{Se}(\text{aq})$	-0.399
$\text{WO}_2 + 4 \text{H}^+ + 4 \text{e} \rightleftharpoons \text{W} + 2 \text{H}_2\text{O}$	-0.119	$\text{In}^{2+} + \text{e} \rightleftharpoons \text{In}^+$	-0.40
$\text{Pb}^{2+} + 2 \text{e} \rightleftharpoons \text{Pb}(\text{Hg})$	-0.1205	$\text{Cd}^{2+} + 2 \text{e} \rightleftharpoons \text{Cd}$	-0.4030
$\text{Pb}^{3+} + 2 \text{e} \rightleftharpoons \text{Pb}$	-0.1262	$\text{Cr}^{3+} + \text{e} \rightleftharpoons \text{Cr}^{2+}$	-0.407
$\text{CrO}_4^{2-} + 4 \text{H}_2\text{O} + 3 \text{e} \rightleftharpoons \text{Cr}(\text{OH})_3 + 5 \text{OH}^-$	-0.13	$2 \text{S} + 2 \text{e} \rightleftharpoons \text{S}_2^{2-}$	-0.42836
$\text{Sn}^{2+} + 2 \text{e} \rightleftharpoons \text{Sn}$	-0.1375	$\text{Ti}_2\text{SO}_4 + 2 \text{e} \rightleftharpoons \text{Ti} + \text{SO}_4^{2-}$	-0.4360
$\text{In}^+ + \text{e} \rightleftharpoons \text{In}$	-0.14	$\text{In}^{3+} + 2 \text{e} \rightleftharpoons \text{In}^+$	-0.443
$\text{O}_2 + 2 \text{H}_2\text{O} + 2 \text{e} \rightleftharpoons \text{H}_2\text{O}_2 + 2 \text{OH}^-$	-0.146	$\text{Fe}^{2+} + 2 \text{e} \rightleftharpoons \text{Fe}$	-0.447
$\text{AgI} + \text{e} \rightleftharpoons \text{Ag} + \text{I}^-$	-0.15224	$\text{H}_3\text{PO}_3 + 3 \text{H}^+ + 3 \text{e} \rightleftharpoons \text{P} + 3 \text{H}_2\text{O}$	-0.454
$2 \text{NO}_2^- + 2 \text{H}_2\text{O} + 4 \text{e} \rightleftharpoons \text{N}_2\text{O}_3^{2-} + 4 \text{OH}^-$	-0.18	$\text{Bi}_2\text{O}_3 + 3 \text{H}_2\text{O} + 6 \text{e} \rightleftharpoons 2 \text{Bi} + 6 \text{OH}^-$	-0.46
$\text{H}_2\text{GeO}_3 + 4 \text{H}^+ + 4 \text{e} \rightleftharpoons \text{Ge} + 3 \text{H}_2\text{O}$	-0.182	$\text{NO}_2^- + \text{H}_2\text{O} + \text{e} \rightleftharpoons \text{NO} + 2 \text{OH}^-$	-0.46
$\text{CO}_2 + 2 \text{H}^+ + 2 \text{e} \rightleftharpoons \text{HCOOH}$	-0.199	$\text{PbHPO}_4 + 2 \text{e} \rightleftharpoons \text{Pb} + \text{HPO}_4^{2-}$	-0.465
$\text{Mo}^{3+} + 3 \text{e} \rightleftharpoons \text{Mo}$	-0.200	$\text{S} + 2 \text{e} \rightleftharpoons \text{S}^{2-}$	-0.47627
$2 \text{SO}_3^{2-} + 4 \text{H}^+ + 2 \text{e} \rightleftharpoons \text{S}_2\text{O}_6^{2-} + \text{H}_2\text{O}$	-0.22	$\text{S} + \text{H}_2\text{O} + 2 \text{e} \rightleftharpoons \text{HS}^- + \text{OH}^-$	-0.478
$\text{Cu}(\text{OH})_2 + 2 \text{e} \rightleftharpoons \text{Cu} + 2 \text{OH}^-$	-0.222	$\text{NiO}_2 + 2 \text{H}_2\text{O} + 2 \text{e} \rightleftharpoons \text{Ni}(\text{OH})_2 + 2 \text{OH}^-$	-0.490
$\text{CdSO}_4 + 2 \text{e} \rightleftharpoons \text{Cd} + \text{SO}_4^{2-}$	-0.246	$\text{In}^{3+} + \text{e} \rightleftharpoons \text{In}^{2+}$	-0.49
$\text{V}(\text{OH})_4^+ + 4 \text{H}^+ + 5 \text{e} \rightleftharpoons \text{V} + 4 \text{H}_2\text{O}$	-0.254	$\text{H}_3\text{PO}_3 + 2 \text{H}^+ + 2 \text{e} \rightleftharpoons \text{H}_3\text{PO}_2 + \text{H}_2\text{O}$	-0.499
$\text{V}^{3+} + \text{e} \rightleftharpoons \text{V}^{2+}$	-0.255	$\text{TiO}_2 + 4 \text{H}^+ + 2 \text{e} \rightleftharpoons \text{Ti}^{2+} + 2 \text{H}_2\text{O}$	-0.502
$\text{Ni}^{2+} + 2 \text{e} \rightleftharpoons \text{Ni}$	-0.257	$\text{H}_3\text{PO}_2 + \text{H}^+ + \text{e} \rightleftharpoons \text{P} + 2 \text{H}_2\text{O}$	-0.508

- 4.5** A nickel indicating electrode is placed in an unknown Ni^{2+} solution and measured against a Standard Hydrogen Electrode (SHE). Given that:



- 4.5.1** Calculate the concentration of Ni^{2+} in the unknown solution in mol/L if the measured voltage is -0.427 V. **(4)**

- 4.5.2** Indicating electrodes actually measure ion activities rather than concentrations. State two conditions under which the activity of ion equals to its concentration. **(2)**

4.5.3 Why is it often necessary to add an ionic strength adjustor, such as potassium chloride (KCl) to the analysis solution before performing oxidation-reduction (REDOX) analyses?
(2)

END OF EXAM

[illegible]

p block														
57	58	59	60	61	62	63	64	65	66	67	68	69	70	71
La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
138.9	140.1	140.9	144.2	144.9	150.4	152.0	157.2	158.9	162.5	164.9	167.3	168.9	173.0	175.0
89	90	91	92	93	94	95	96	97	98	99	100	101	102	103
Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr
227.0	232.0	231.0	238.0	237.0	239.1	243.1	247.1	247.1	252.1	252.1	257.1	258.1	259.1	260.1
f block														